Principles of Electronic Nanobiosensors

Unit 3: Sensitivity
Lecture 3.3: Potentiometric Sensors:
Charge Screening for Cylindrical Sensors

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Outline

• Recall: Salt and screening
• Theory of screening for a Cylindrical NW sensor
• Comparison with experiments
• Special issues of small sensors
• Conclusions
Recall: Salt screening for Planar Sensor
Screening different for 1D sensors?

Geometry of diffusion was different, what about screening?
**Cylindrical NW sensor**

\[ L_D + a + t_{ox} \]

\[ Q_{NW} = \frac{C_{ox}}{C_{ox} + C_{DL}} Q_{bio} \]

\[ L_D^2 = \frac{\kappa_w \varepsilon_0 k_B T_L}{2 z^2 I_0 N_{av} q^2} \]

\[ C_{ox} = \frac{2 \pi \kappa_{si} \varepsilon_0}{\ln\left[1 + \left( t_{ox} / a \right) \right]} \]

\[ C_{DL} = \frac{2 \pi \kappa_w \varepsilon_0}{\ln\left[1 + \left( L_D / a + t_{ox} \right) \right]} \]

Does offer some advantage!
Cylindrical NW sensor: at high salt density

\[ \beta = \frac{zeq}{k_B T} \]

\[ Q_{bio} = \sigma_T N(t) \]

\[ Q_{DL} = -\frac{2k_w \varepsilon_0}{\beta L_D} \sinh \left( \frac{\beta \psi_0}{2} \right) \left( 1 + \frac{\gamma^{-2} - 1}{\cosh^2 (\beta \psi_0 / 2)} \right)^{1/2} \]

\[ Q_{NW} = -\frac{2\pi \kappa_{ox} \varepsilon_0}{2\pi (a + t_{ox}) \log (1 + t_{ox}/a)} \Psi_0 \]

\[ \gamma \equiv \frac{K_0 (bL_D^{-1})}{K_1 (bL_D^{-1})} \]
NW sensor: at high salt density

\[ Q_{DL} = -\frac{2k_w\varepsilon_0}{\beta L_D} \sinh(\beta \psi_0 / 2) \left( 1 + \frac{\gamma^{-2} - 1}{\cosh^2(\beta \psi_0 / 2)} \right)^{1/2} \rightarrow -\frac{k_w\varepsilon_0}{\beta L_D} e^{\beta \psi_0 / 2} \]

\[ Q_{bio} = Q_{NW} + Q_{DL} \sim Q_{DL} = -\frac{k_w\varepsilon_0}{\beta L_D} e^{\beta \psi_0 / 2} \]

\[ Q_{bio} = \sigma_T N(t) = \sigma_T \rho_0 t_s^{(3-D_F)/2} \]

Alam, Principles of Nanobiosensors, 2013
NW sensor: same result, different constants

Almost point by point screening .... Like the planar sensor

\[ \frac{k_w \varepsilon_o}{\beta L_D} e^{\beta \Psi_0/2} = \sigma_s \rho_0 t_s^{(3-D_F)/2} \]

\[ L_D^2 = k_r \varepsilon_0 k_B T_L / 2 z^2 I_0 N_{av} q^2 \]

\[ S(t) = \frac{\Delta G}{G_0} = \frac{2 Q_{NW}}{q N_D a} = \frac{2 k_{ox} \varepsilon_0 \psi_0}{q N_D^2 \log(1 + t_{ox}/a)} \]

\[ S(t) \propto \frac{Q_{MOS}}{q N_D a} = c_1 \ln(\rho_0) + c_2 \frac{(3 - D_F) \ln(t)}{2} - c_3 \ln(I_0) + c_4 \]

Alam, Principles of Nanobiosensors, 2013
Screening limited response

Bunimovich et al., JACS, 2006
Cheng et al., COCB, 2006
Zheng et al., Nat Biotech. 2005

Cui et al., Science, 2001
Hahm et al., NanoLett., 2004
Lud et al., CPC, 2006

\[ S(t) \sim c_1 \left[ \ln(\rho_0) - \frac{\ln(I_0)}{2} + \frac{\ln(t)}{D_F} + \alpha[pH] + c_3 \right] \]

Experimental [7]
Simulations
\[ k_f = 3 \times 10^7 \]
\[ k_R = 0.1 \]
\[ N_0 = 10^{13} \]
\[ I_0 = 10^{-9} \]

Experimental [1]
Simulations
\[ k_f = 3 \times 10^8 \]
\[ k_R = 10 \]
\[ N_0 = 10^{13} \]
\[ I_0 = 10^{-5} \]
\[ D = 1.6 \times 10^{-8} \]
Discussion: Salt and screening

$$U = -\frac{q^2}{4\pi\varepsilon_0 r} \times \frac{1}{k_B T_L} \sim k_B T_L$$

$$n^- \sim I_0 N_{av} e^{+q\psi/k_B T_L}$$

$$n^+ \sim I_0 N_{av} e^{-q\psi/k_B T_L}$$
Issue 1: Screening reduces the distance you can see

\[ Q_1 = \frac{C_{ox}}{C_{ox} + C_{DL}} Q_{bio} \]

\[ \frac{k_{ox} L_D}{k_w T_{ox}} \rho_0 \quad (L_D \sim T_{ox}) \]

\[ L_D^2 = \kappa_w \varepsilon_0 k_B T_L / 2z^2 I_0 N_{av} q^2 \]

Increase in salt density reduces the distance you can see
Issues 1: You cannot see the full DNA Screening in 2D (NW sensors)

\[ Q_{MOS} = C_0 \frac{Q_{bio}}{C_0 + C_{DL}} \quad \iff \quad L_D = \sqrt{\frac{\kappa_w \varepsilon_0 k_B T_L}{2z^2 I_0 N_{av} q^2}} \]

Hybridization efficiency \( \delta = 1.0 \)
Manning coefficient \( \theta = 0.75 \)
\( b = 0.34 \) nm/per turn of DNA

\[ Q_{bio} = N \times q \left( L_D / b \right) \times \delta (1 - \theta) \]
Issue 2: Distributed vs. localized charge

We assumed charges are distributed, but they are actually discrete … Was the theory developed all wrong?
Importance of fluidic environment

Water is a high-k dielectric, it spreads the charge over the NW sensor.
Issue 3: Doping is discrete

Random Dopant Fluctuations

Smaller diameter and doping density
better sensitivity!

Issue 4: Faradic vs. non-Faradic electrodes

Non-Faradic

\[ \psi = \frac{C_1}{C_1 + C_2} V_G \]

Faradic

\[ \psi \approx V_G \]

Ohmic, Faradic contact to define fluid potential
Conclusions

• Potentiometric sensors rely on charges of biomolecules for detection
• At low concentrations, NW screening is very different from screening of planar sensors. The difference disappears at higher concentrations.
• The doping type of the sensors must be chosen carefully for maximum sensitivity.
• Water and oil have very different charge distribution pattern on the channel, with different responses to the same biomolecules.
• It is extremely important to use Faradic electrodes for measurements. We will explain why, during discussion of amperometric sensors.
Review questions

• If I increase salt concentration by a factor of 100, by how much will the sensitivity reduce?
• Explain physically, why the response increases logarithmically although the biomolecules arrive linearly?
• Is a cylindrical sensor more sensitive than a planar sensor?
• Is distributed charge approximation justified if the experiments were done in oil?
• What is wrong with using non-Faradic electrode?
• Is it true that biosensors are most sensitive to depletion? What type of NW doping would you use for DNA?